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PHASE COMPOSITION, STRUCTURE AND PROPERTIES OF THIN FILMS BASED ON THE DOUBLE OXIDE SYSTEM ZrO_2–GeO_2

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The phase composition, structure and properties of ZrO_2–GeO_2 thin films obtained by the sol-gel method from the film-forming solutions based on zirconium oxochloride $ZrOCl_2 \cdot 8H_2O$, germanium tetrachloride and ethyl alcohol are studied. The physical-chemical properties of the films obtained as functions of their composition are determined and the composition–property diagram are constructed.

Key words: sol-gel method, film-forming solution, thin film.

Thin-film nanostructural materials are of great value in modern technology, the electron and electric engineering industries and the construction industry. They find wide applications as light-redistributing and interference filters and protective and dielectric coatings. Accordingly, thin films as promising materials must possess stable properties in comparatively tough operating regimes and be comparatively inexpensive and technologically adaptable [1, 2]. Of the currently used materials zirconium dioxide thin-films obtained by the sol-gel method from film-forming solutions best satisfy these requirements [3, 4]. However, for films based on zirconium dioxide it is necessary to take account of its modifications which change the characteristics of the material in the course of operation, and for this reason oxides of other elements are introduced in order to stabilize the structure and therefore the properties. In so doing it is possible for solid solutions based on the cubic modification of zirconium dioxide or chemical compounds whose properties differ fundamentally from those of pure oxides to form [4, 5]. For this reason the objective of the present work was to obtain thin films based on the double oxides ZrO_2–GeO_2 by the sol-gel method from film-forming solutions in the entire range of concentrations and to study the phase composition, structure and properties of the films obtained.

The thin films were synthesized by the sol-gel methods from film-forming solutions (FFS), which were based on ethyl alcohol (96 wt.%), ultrapure germanium tetrachloride $GeCl_4$ and analytically pure zirconium oxochloride $ZrOCl_2 \cdot 8H_2O$ with total concentration 0.4 moles/liter. The film-forming solutions were kept at 25°C for a definite period of time in order to allow the solution viscosity to reach a value from 2.3×10^{-3} to 5.5×10^{-3} Pa · sec. The films were obtained on glass, single crystal silicon and quartz substrates by centrifuging and drawing with rotation speed of the centrifuge 500 – 3000 min^{-1} and pulling rate 1 – 5 mm/sec. The films were formed in two stages in air in a drying cabinet at temperature 60 – 80°C and in a muffle furnace at temperature 500 – 900°C.

The infrared spectra of films on silicon substrates fired at different temperatures were recorded in the frequency range 400 – 4000 cm^{-1} with a Perkin Elmer Spectrum One spectrophotometer. The phase composition of the synthesized films was determined with a DRON-3M diffractometer using a characteristic copper anode CuK_α (λ = 1.5418 nm). The adhesion of the films to the substrate was measured with a PMT-3 microhardness tester. The optical characteristics of the films (refractive index and thickness) were investigated with a LÉF-3M (λ = 632.8 nm) laser ellipsometer. For each sample measurements were performed at five points along the surface of the films and the optical parameters were calculated in a model of a uniform nonabsorbing layer on an isotropic substrate [6]. The reflection and transmission spectra of the films in the visible and UV ranges were obtained with a SF-20 spectrophotometer. The values of the permittivity were calculated by the Kramers–Kronig method using the reflection and transmission spectra, and the band gap was determined according to the position of the transmission edge. The electrophysical properties of the films obtained were studied with an E7-8 apparatus. A 673M pH meter was used to study the acid-base properties. An atomic-force microscope (NT-MDT Ntegra Aura) with silicon needle diameter 2 – 5 nm was used to study the surface and mechanical properties of the experimental films.

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TABLE 1. Assignment of IR Bands of Films Before and after Firing

Film composition	Vibration type	Wavenumber, cm^{-1}	
		pre-firing, $t = 25°C$	post-firing, $t = 700°C$
GeO_2	(O–Ge–O)	720	701, 582
	ν(Ge–O–H)	3264	3147
	$\nu(OC_2H_5)$	2920, 2844	–
	$\delta(OC_2H_5)$	1450	–
	ν(H–O–H)	3360	–
	δ(H–O–H)	1630	1619
ZrO_2	(O–Zr–O)	620	–
	ν(Zr–OH)	1090	–
	$([ZrO_2]^{4+})$	–	871, 584
	$\nu(OC_2H_5)$	2922, 2844	–
	$\delta(OC_2H_5)$	1400	–
	ν(H–O–H)	3400	–
	δ(H–O–H)	–	–
GeO_2–ZrO_2	ν(Ge–O–H)	3264	–
	ν(Zr–O–H)	1090	–
	(Zr–O–Ge)	–	1045, 630
	$([ZrO_2]^{4+})$	–	813
	(O–Ge–O)	585	–
	(O–Zr–O)	671	667
	$\nu(OC_2H_5)$	2900, 2844	–
	$\delta(OC_2H_5)$	1400	–
	ν(H–O–H)	3400	
	δ(H–O–H)	1630	–

To obtain films with a uniform composition and thickness and quite strongly bonded to the surface of the substrate the film-forming solution must contain the optimal ratio of the initial film-forming material and solvent. At the same time this ensures, on the one hand, fast partial hydrolysis and polymerization in solution with the products formed being maintained in the form of a sol and, on the other hand, final hydrolysis in a thin layer during FFS deposition on the substrate [1]. It was established experimentally that film formation occurs only after maturation of the solution and the viscosity of the FFS for obtaining films which have uniform thickness and good adhesion to the substrates must lie in the range from 2.3×10^{-3} to 5.5×10^{-3} Pa · sec. As a result single-layer films of the double oxide system ZrO_2–GeO_2 with molar content ranging from 0 to 100% were obtained from such solutions and the phase content, structure and properties of the films were studied.

The films obtained on glass substrates are x-ray amorphous for all compositions with no exceptions. The data from IR spectroscopic (Table 1) and x-ray phase (Table 2) analyses showed that a GeO_2 film on silicon substrates fired at temperature 900°C for 12 h are an amorphous modification, which is in agreement with the results presented in [7].

TABLE 2. Phase Composition of Films with Different Firing Temperatures (from XPA)

Molar content of samples, %	Firing temperature, °C		
	500	700	900
ZrO_2	C + T	T + M	M
90% ZrO_2, 10% GeO_2	C + T	C + T	C + T
70% ZrO_2, 30% GeO_2	A	T	S + T
50% ZrO_2, 50% GeO_2	A	T	S + T
30% ZrO_2, 70% GeO_2	A	T	S + T
GeO_2	A	A	A

Notations: C) cubic; T) tetragonal; M) monoclinic modification of ZrO_2; S) tetragonal structure of scheelite $GeZrO_4$; A) x-ray amorphous.

X-ray phase analysis of ZrO_2 films obtained on silicon substrates shows that at 500°C the zirconium oxide film formed has cubic and tetragonal modifications and as temperature increases a transition occurs from tetragonal into monoclinic. This transition is completed at 900°C (see Table 2). The absorption bands, corresponding to vibrations of water and –OH groups, in the IR spectra vanish with increasing temperature. Degradation of the film-forming solutions on the surface of the substrate is accompanied by polymerization and formation of infinite chains of the form –Zr–O–H with frequency 1090 cm^{-1} and –Zr–O–Zr– with vibrational frequency about 620 cm^{-1}.

At temperature close to 700°C a regular ZrO_2 crystal lattice forms and bands corresponding to the formation of chains vanish in the IR spectra and vibrations of ZrO^{4+} tetrahedra appear near 871 and 584 cm^{-1}, which indicates crystallization in the films.

At low molar content of GeO_2 (to 10% in the films) stable cubic and negligible amounts of the tetragonal modification of ZrO_2 are present at temperatures from 500 to 900°C. This indicates that these films are structurally stable and therefore their properties are stable.

For the compositions ZrO_2–GeO_2 with germanium oxide molar content from 30 to 70% identical peaks attesting to the formation of the chemical compound zirconium germanate with the general formula $ZrGeO_4$ of the tetragonal modification with scheelite $CaWO_4$ structure are present and a second phase corresponding to the tetragonal modification of ZrO_2 is also observed. The formation of the chemical compound with such a composition for systems consisting of volume phases is described in [8, 9].

The results of atomic force microscopy studies of ZrO_2–GeO_2 thin-film systems with 50 mole % GeO_2 are presented in Fig. 1. The studies were performed in surface topography and phase contrast regimes. The latter method is used to study heterogeneous structures and makes it possible to measure, in addition to the topography, the mechanical

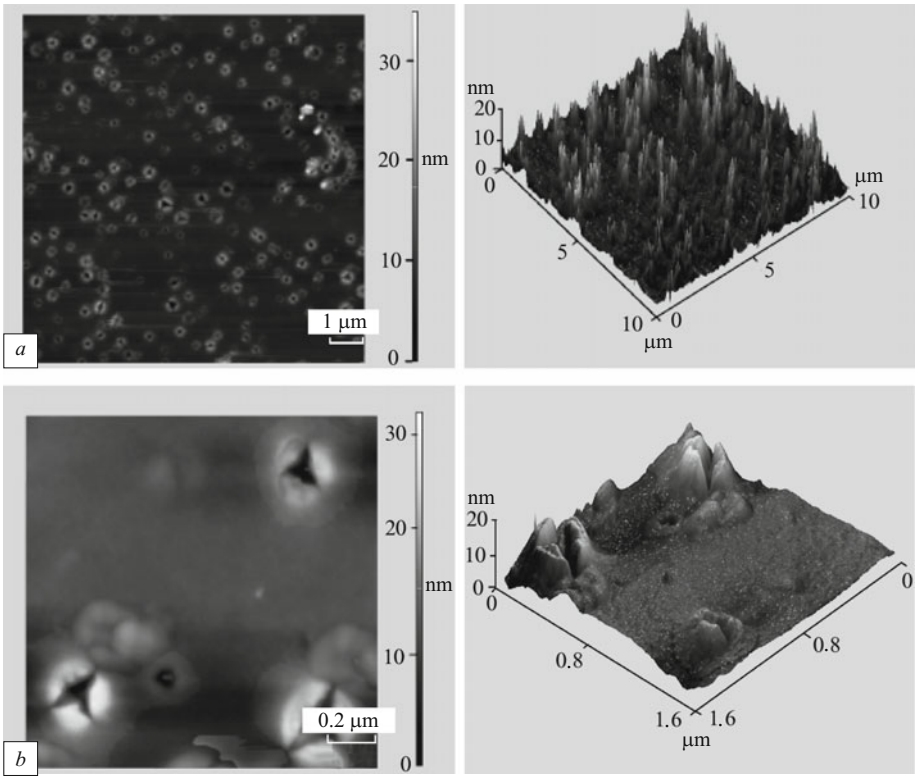

Fig. 1. AFM images of the surface of ZrO_2–GeO_2 films, obtained in phase contrast (*a*) and surface topography (*b*) regimes.

properties of the surface layer and to confirm the presence of different phases [10]. The results showed nonporous, continuous and uniform films consisting of two phases with ordered fractal structure in the form of ring and rod formations with ring size in the range 50 nm and projection height 2.6 nm.

The optical, acidic and electrophysical properties of films of interest for practical applications as well as adhesion of the films to different substrates were studied in the present work. A structure-sensitive parameter — the index of refraction — as well as the surface acidity were taken as the properties for constructing the diagram of the system ZrO_2–GeO_2. The composition–property diagram is presented in Fig. 2 and the main properties of the films obtained on the silicon substrates are presented in Table 3.

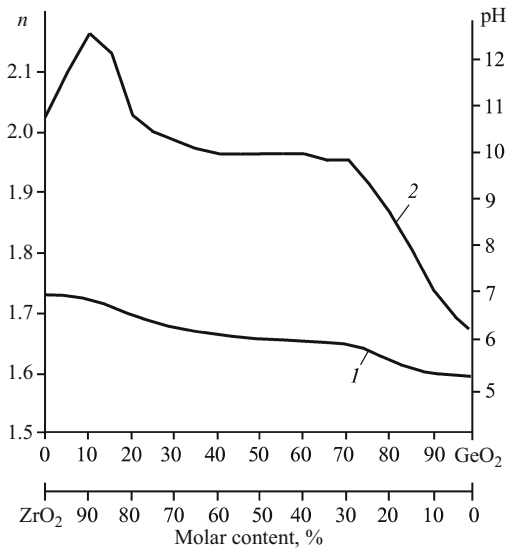

Fig. 2. Composition–property diagram for ZrO_2–GeO_2 films: *1*) acidity (pH) of the suspension; *2*) refractive index (firing temperature 900°C).

For ZrO_2–GeO_2 composition with germanium molar content to 10% the refractive index increases sharply to 2.16. This is due to the formation of a solid solution based on the cubic modification of ZrO_2. It was found that for GeO_2(ZrO_2) molar content from 30 to 70% a chemical compound forms; this is also reflected in the properties of the films obtained. The refractive indices in compositions with the formation of a chemical compound have approximately the same value 1.95 – 1.97. The acidity diagram shows that the acidity increases evenly with increasing germanium oxide content; in addition, as the GeO_2 molar content increases from 30 to 70% the pH remains in the range 6.2 – 6.0.

The film thickness ranges from 65 to 94 nm. Thicker films are obtained for germanium oxide; this is due to the higher viscosity in FFS. GeO_2 films have the lowest and ZrO_2 films the highest adhesion; this is because the ionic fraction of the bond for zirconium dioxide is higher than for germanium oxide, so that the adhesions is better between zirconium oxide and silicon substrates.

Depending on the composition the resistivity of the films obtained is 10^8 – 10^{12} Ω · cm, the band gap 1.69 – 2.16 and the rf permittivity 5.52 – 11.35.

TABLE 3. Physical-chemical properties of ZrO_2–GeO_2 films.

Parameter	Film composition							
	ZrO_2	GeO_2	GeO_2 molar content in ZrO_2–GeO_2 film, %					
			5	10	30	50	70	90
Film thickness, nm	60	94	65	68	77	78	82	88
Refractive index, *n*	2.03	1.69	2.11	2.16	1.97	1.96	1.95	1.72
Adhesion *F*, MPa	1.93	0.86	1.87	1.85	1.65	1.63	1.60	1.08
Permittivity ε	8.16	5.52	10.12	11.35	7.22	6.71	6.20	5.85
Band gap *E*, eV	5.1	4.5	4.8 – 5.0					
Resistivity ρ, Ω · cm	10^{10} – 10^{12}	10^{8} – 10^{10}	10^{9} – 10^{12}					

CONCLUSIONS

In summary, films based on the double oxides ZrO_2–GeO_2 were obtained from film-forming solutions with different composition. Property–refractive index and property–acidity diagrams were constructed for this system. The films made by means of the technology developed have high chemical and thermal resistance, adhere well to different substrates and are wide-band semiconductors. The thickness of the films ranges from 60 to 94 nm depending on their composition.

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